

Welding Metallurgy
Prof. Pradeep K. Jha
Department of Mechanical and Industrial Engineering
Indian Institute of Technology – Roorkee

Lecture - 27
Solute Redistribution During Solidification

Welcome to the lecture on Solute Redistribution during Solidification. So many a times we come across the terms known as Chemical inhomogeneities so especially during the weld microstructure. So pertaining to the discussion on solidification topic we will talk about the solute redistribution issues which occur during the solidification because when a liquid of you know certain composition, certain solute composition that solidifies.

Then basically it is all by the you know by the process of nucleation of you know solid and then there will be nucleation and then further there will be growth. So you will have solid which is coming out seldom it is you know when you are talking about the alloys with freezing range in those cases the solid as well as the liquid composition they will be changing and that leads to the cases of homogeneities depending upon many factors. So in this lecture we are going to discuss about those issues and have some idea about them.

(Refer Slide Time: 01:50)

Introduction

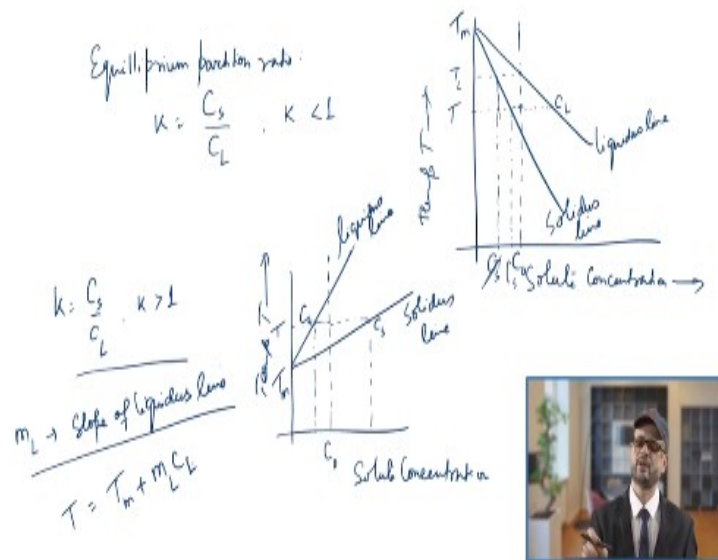
- When a liquid of uniform composition solidifies, the resultant solid is seldom uniform in composition.
- The solute atoms in the liquid are redistributed during solidification.
- The redistribution of the solute depends on the phase diagram, diffusion, undercooling, fluid flow, and so on.

So when a liquid of uniform composition solidifies the resultant solid is seldom uniform in composition because you will have we will discuss that in case of alloys when we talk so in those cases you have the solid which is coming out it will have different composition than the liquid. So the solute atoms in the liquid are redistributed during the solidification and this

redistribution of the solute that will be depending upon the phase diagram diffusion under cooling fluid flow and so on.

So these are the factors basically which basically define that how there will be the redistribution of the solute.

(Refer Slide Time: 02:40)



So coming to you know the about the we have already talked about the phase diagram and what we have seen that when we see the solidification of certain binary alloys. Now in this case as we know that when you have the solidification so if suppose you have the melt of this composition, so this is your solute concentration. So if your melt is having this concentration C_0 . Now as you know that when you are so this temperature is the T_m .

Now when you come to this temperature this is the liquidus temperature and this temperature will be known as T_L for this composition. Now what happens that at this temperature the solid which is formed so this is solid concentration in this direction and this is basically the temperature T . So at this point at this liquidus point at this point the solid which will be formed it will have the composition and this is defined as the concentration of the solid.

So this is known as C_s . Now at this point the liquid is having that concentration C_0 . Now as you go you know further down so suppose you are coming to any temperature T so if you talk about this point which is having the temperature T . Now at this point as you know the C_s which was here now at this point this will be your C_s this will be the concentration of the solute you know solid having solute in the solid.

So basically this C_s will be varying along this line so you can remove this so if you talk about a particular temperature you know at temperature T at this T temperature this solid which is crystallized out it will have the concentration C_s and similarly you will have you know you are coming to this line so if you are having you know this horizontal line drawn from here. So we have already seen that this composition is known as C_L so C_L is C_0 at $T = T_L$.

However, as we come down so this C_L will go on you know following along this line so this will be your C_L . So this is your solidus line and this is known as the liquidus line. So the concentration you know solid so it will be following concentration of this solid which is crystallized it will follow this line and of the liquid it will follow this line. Now if you talk about a term so there is a term known as the you know equilibrium partition ratio.

So the equilibrium partition ratio so this is defined by, you know, the ratio of C_s to C_L so this K will be C_s/C_L . Now as you know in this case the $C_s < C_L$ so in such cases your K value will be smaller and it will be < 1 . Now if you talk about you know another kind of you know phase diagram where you know the phase diagram goes like this. Now in this case what we see that if you know come to any composition C_0 .

Now in this case again you have the temperature T is going like this and this is your solute concentration. So in this case as you come down so if you talk about you know at any temperature T so this will be your you know T_m and at any temperature T so if you talk about T so this is your solidus line and this is your liquidus line. So in this case you will have you know C_s touching to this point.

So this will be you know corresponding to C_s and this will be corresponding to C_L . Now what we see in this case is C_s is I mean having a larger value than C_L so solid which is crystallizing out it will have the solute concentration more than what the liquid has and it continues to grow you know as we come down it continues to fall down basically in this case you know it will follow.

So as you decrease the temperature this C_s value as well as C_L value they both will be decreasing with time whereas in this case you know C_s and C_L both increase with time, but if in this yes if you talk about the equilibrium partition ratio C_s/C_L so in this case $K > 1$. So as

you see that there are two cases one is $C_s < 1$ and another is $C_s > 1$. So if you define the slope of this liquidus line as m_L .

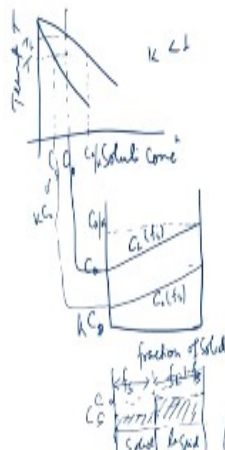
So if m_L is the slope of liquidus line in that case you can you know because slope is you know < 1 in one case in this case it is < 1 because this angle $\neq \theta$ is more than 90 and in this case slope is you know > 1 more than you know it is positive one is positive and one is negative. So in that case you can have the expression for the temperature T on the liquidus line.

So if you have any temperature T in the liquidus line will be $T_m + m_L \cdot C_L$. So that is how you know you can have the calculation of the T you know in any case. Now we will talk about you know the different cases when you have the difference of diffusion. So this was related to the phase diagram and also we defined these equilibrium partition ratio which we basically will be talking about the ratio of C_s and C_L .

Now we will see that you know depending upon the different diffusion rates in the solid and in the liquid how you know the different cases arise.

(Refer Slide Time: 11:00)

Complete diffusion in solid & liquid



$k < 1$

$C_s f_s = C_L f_L \rightarrow$ amount of solute in solid & liquid

$C_0 (f_s + f_L) \rightarrow$ amount of solute in liquid before solid fraction

$C_s f_s + C_L f_L = C_0 (f_s + f_L) = C_0$

$f_s = 1 - f_L$

$f_L = \frac{C_0 - C_s}{C_0 - C_L}$

$f_s = \frac{C_0 - C_L}{C_0 - C_s}$


$C_s = \frac{C_0}{f_s + k(1-f_s)}$

$f_s = \frac{C_0 - C_s}{C_0 - C_L}$

$f_L = \frac{C_0 - C_s}{C_0 - C_L}$

$D_s t \gg l^2$
 $D_s \rightarrow$ diffusion coeff. of solute in solid

$D_L t \gg l^2$



So we will talk about a case in which there is complete diffusion in solid and liquid. So if there is a case of complete diffusion in solid and liquid so basically that makes you know to understand that in these cases you will have the solid or liquid of uniform composition you will be getting. If there will be complete diffusion in solid and liquid because there will be redistribution of the atoms at the interface you know solute which is coming out it will have lesser.

You know so once if you come to the lower temperature then all these solid phases which are there so they basically will be redistributing the atoms. So in those cases how these you know how you get these how it looks like the how can you show it you know this solute redistribution in those cases. So you know suppose you are taking for a case so first of all this will happen you know in these cases you will have the condition so in the case of the, you know, dissolution in the solute or solute diffusion.

So for that basically in the solid state the condition will be $D_s t \gg l^2$. So basically D_s will be the diffusion coefficient of the solute in solid. So and similarly you will have the diffusion coefficient of the liquid also. So in liquid case you should have again $D_l t \gg l^2$. So as l is the initial length of the liquid in this case. So these are the conditions you know so these you know this is rate this is time.

So basically that should be quite higher than these distance through which it has to diffuse. So these are the conditions and certainly depending upon the D_l and D_s values you know the diffusion rate will vary. Now the thing is that when you have a case of complete solid you know diffusion in solid and liquid. So in that case your how it varies. So suppose as you have seen you have going like this, this will be your solute concentration.

So this line the x-axis you have solute concentration and this way you have the temperature. Now as you know that in this case that if suppose you are coming to this C_0 concentration now at this temperature T . So you know so this will be your T_L that is your liquidus temperature this is your at defined temperature T and now this will be so at this point where it is touching you will have this as the C_s .

And similarly you will have so this is your C_L so it will be $K C_0$. So this will be basically $K C_0$ so C_s will be nothing, but $K C_0$ and this is C_L so that will be C_0/K . In this case basically the K value is < 1 so that is why this will be C_0/K . Now in this case so as you see that this is your $K < 1$ and this is your initial melt composition that is C_0 . Now what happens that in such cases if you look at the you know C_L and C_s .

So what you see that if you draw so this line this will be C_0 and this C_0 which is you know the coming for the liquid so this C_0 basically. So from here this line will move and it will go up to

C_0/K . So this is for the you know C_L value as you know that this for liquid this value will be moving this is C_0 so at T_L your this C_0 is C_L and then so here you have this C_0 and then it will be you know so it will be moving and this will be coming to this C_0/K .

So ultimately your this value is C_0/K . So you know you are coming finally to C_0/K so this will be your C_0/K . For the liquid it starts from C_0 and goes to C_0/K . For the solid it will be starting from C_s and then it will be you know say this C_s line will go and ultimately it will come up to C_0 so if this becomes C_0 then for C_s so this line basically will be coming as C_s and here from you will have this line moving up to so it will be touching finally this line.

So your this will be your C_s that is for the solid and this will be you know since it is also depending upon the solute concentration only so this is $C_L(f_s)$. So this will be your if you look at in this case this is this axis is fraction of solid and as the fraction of solid varies you know it varies from you know this value that is this is KC_0 so this is nothing but this is kC_0 and this KC_0 to C_0 and then C_0/K it is going.

Now if you look at the total volume of material which is formed in such cases. So if you try to draw this you know graph again so what is happening is that if suppose this is the solid form so some part is you know this is solid and this is your liquid which is you know liquid part. Now as you may have seen that for the solid you will have the you know you will have C_L so this is your C_s and from C_s it will go up to C_0 and similarly so this is your C_0 and for the liquid it will be moving. So it will be going from here to further to this value.

So this part is the fraction of solid and this will be the fraction of liquid. The fraction of liquid is nothing, but $1 - f_s$. So basically $f_s + f_L = 1$. So you know you will have the if you look at the solid part it will be this part will be solid and you will have this part as the liquid and your solid at the end will have the composition C_0 so you will have the uniform composition C_0 all throughout.

Now if you have you know if you look at the hatched areas now you have you know $C_s(f_s)$ and the $C_L(f_L)$. Now these are the amount of solute so they are the respective amount of solute there will be amount of solute in solid and liquid. So the amount of solute in solid and liquid. Now if you see you know the so f_s and f_L we know that this is a fraction of solid and the liquid. Now the area that is form composition, C_0 . So $C_0(f_s + f_L)$.

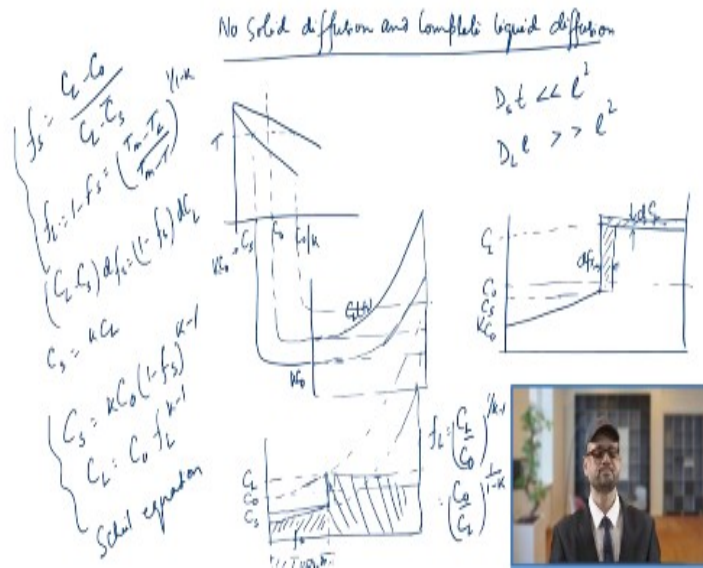
So this so this will be you know the amount of solute in liquid before solidification. So if you know equate you will have $C_s f_s + C_L f_L$ that will be you know $C_0 (f_s + f_L)$. So $f_s + f_L$ is 1 so you will have that is known as C_0 . So if you substitute you know $f_s = 1 - f_L$ so in that case you can have the you know lever rule so that is formed that is $f_L = (C_0 - C_s) / (C_L - C_s)$ that is the equilibrium lever rule which is obtained.

Similarly, you get the f_s and f_L you get as a $(C_L - C_0) / (C_L - C_s)$. So this is what you get in the case of complete diffusion in solid and liquid and you also get the composition of liquid you can have the expression for the composition of liquid C_L and that can be formed you know found out by $C_0 / (f_L + K(1 - f_L))$. So depending upon the value of K you know the equilibrium partition ratio in terms of that and fraction of liquid and for the particular composition you can have the, you know, concentration of that liquid portion that can be found out.

And they basically help us in you know predicting many things like how that C_L will be changing based on that how you know the liquidus temperature line will be changing because as we know that as there is decrease in the temperature in those cases you will have the change in the liquidus temperature line. So based on that there will be few more you know events happen a few more phenomena occurs like what we will discuss in our coming lectures.

So because of the problem in the solute redistribution. So this is for those cases where you have complete diffusion in solid and the liquid. Now if you may have a case where you will have the you know diffusion in the liquid is there, but diffusion in the solid is not complete. So we do not have the diffusion in solid, but you have the complete diffusion in liquid.

(Refer Slide Time: 23:25)



So you may have the case of no solid diffusion, but you have a complete liquid diffusion. Now in this cases basically for them the condition is that if the condition is such that your $D_s.t$ is quite $< l^2$ if you know this distance is quite larger in that case it means that diffusion in the case of solid is quite small whereas the $D_l.t$ so this is quite $> l^2$. So in such cases you know when your diffusion in that solid you know case is solid state is quite small.

So in those cases you know such conditions are faced and how you know so what will happen that you will have the equilibrium only you know case only on the interface because inside this solid there is no redistribution, there is a diffusion is not so fast so you do not have the you know uniform composition in the case of solid. So in this case solute cannot diffuse back you know into the solute into the solid and so it will reject it will be rejecting these you know solute and that has to go into the liquid.

So in fact for the liquid basically the concentration in the liquid portion the concentration in the liquid of the solid will go on increasing and since from this liquid only the solid has to come out. So since its concentration will go on increasing so the solid which is formed later on it will have its concentration will also go on increasing. So that way your you do not have uniform composition of this solid which is forms at the end of the solidification if you look at the solid phase you do not have the uniform basically composition of solute.

So if you look at you know it is a case so what happens that if you see this is the case now in this case again we are coming to this concentration as C_0 and then at least this is the temperature T so you will have this as the line C_s and so this will be you know so it will be

nothing but KC_0 and when it is drawn horizontally and it is touching this liquidus line so it will be C_0/K .

Now as we discussed that in these cases you know these concentration if you look at you know we have completely liquid diffusion in the liquid whereas no such case in the case of solid. So if you draw so your this C_s will be you know coming and this is your case KC_0 so you know this is your KC_0 and this is your C_0 so C_0 is mapped here. Now this will be C_L so this C_L basically it will be moving to a very large value than C_0/K because of the very high value of diffusion in case of liquid and there is very poor value in the case of solid.

So your C_L f_s line this will be going quite more than this. So you will have this C_0/K value is here, but it goes quite past this and since this liquid only from this only because it has a larger concentration of solute. So from there only the solid is formed so solid also in the later part it will also go and it will also move and it will be reaching also it will have the larger concentration value towards the end.

So this way you know if you look at the fraction of solid and the liquid so in this case if suppose we talk about the solid and liquid form. So what happens that you will have the you know this is your C_s line and this is basically if you talk about in the bottom if you talk about this as the solid portion so this is your solid. Now this is so here also it is decreasing and coming to C_s suppose this is instant so your this is your, this will be your hatched line that is your solid.

And then so and this side you will have the liquid so here you will have larger concentration so this will be your, you know, C_L and in between you have C_0 . So now because of that you will have you know this is your liquid part. So now in this case you will have the movement from here it goes and for the you know liquid it will be moving from here and then you will have larger concentration at this point and it will go further so that is what we have seen.

So if you talk about the cases in such case so what happens that this is your f_s so we will have you know f_s on this side. So basically you will have the some of these hatched area there will be you know amount of solute in the liquid before solidification. So what happens that if you look at you know further this is what we see that you will have this area going and from here so you will have the increase in this zone.

And on this side you will have you know increasing this f_s so this distance is taken as df_s and this is taken as dC_L so you know so in those cases what we take is that you know did this hatched area will be equal to the amount of solid solute in that before the solidification. So you know hatched area 1 will be equal to 2 so based on that so you will have one is increasing this area and another is increasing this area.

So you will have you know C_0 coming up here then you will have KC_0 here this is your, you know, this is your C_s so that way same expression comes out and this is your you know C_L . So then in that case if you equate so what we get in these cases if you try to find the expression so your expression becomes $C_L - C_s$ into you know Df_s so that will be $= (1-f_s)dC_L$.

So basically you know this increase in area should be equated to this increase in area so that will be your so if you equate that so df_s and this will be $C_L - C_s$ so that this area will be $= dC_L$ into you know $1-f_s$ because this will be your f_L so that is how. Now in this case again if C_s is taken as KC_L and if you integrate these equations $C_L = C_0$ at $f_s = 0$ so in those cases what you get is the equation which you get is C_s will be we are getting a $C_s = KC_0(1-f_s)^{K-1}$ or you also get C_L as $C_0 f_L^{K-1}$.


So these two equations which you are getting to find this C_s and C_L they are known as the Scheil equation so these are the Scheil equation. So this is you know the solute redistribution equation you know they are representing the solute segregation you know when you have the no proper solid diffusion and you have complete liquid diffusion and from here you can find you know the values like you may have the expression for f_L as $(C_L/C_0)^{1/K-1}$ or you can also write $(C_0/C_L)^{1/1-K}$.

And then you know in these cases you have since you have not a uniform you know composition of the solute in the solid case so you get the expressions for the you know f_s as $C_L - C_0$ from the equilibrium lever rule and you get $C_L - C_s$ bar so that is known as the average you know composition of the solid that is C_s . So from here you get a large many equations, but this basically is giving you the concept about you know the case where there is no solute diffusion is there in the solid.

And you have the complete liquid diffusion and we can have expressions for f_L also f_L will be $1-f_s$ so you will have $(T_m-T_L / T_m-T)^{1/(1-K)}$ because we are getting $(T_L-T_m/C_0) = m_L$ because we know the slope of the liquidus line which is assumed you know a straight line. So in those cases you can have the different expressions for f_s f_L and all that can be found out.

(Refer Slide Time: 35:05)

No solid diffusion & limited liquid diffusion




Solute rich boundary layer

Cp < C0

Solute rejected gets piled up & forms a solute rich boundary layer ahead of growth front.

$$\frac{C_L - C_0}{C_0/k - C_0} = e^{-(R/D_L)z}$$



There is another case where you will have you know the no solid diffusion and you have limited even the liquid diffusion. Now in such cases what is happening that you will have the solute buildup at the interface and because here you will have again this is in this case you have only liquid limited liquid diffusion is there. So again in these cases if we try to understand through the phase diagram.

So what will be happening again here in this case you will have because here because of the no solid diffusion and limited liquid diffusion you will have convection also is assumed negligible. So you will have neither the solid nor the liquid of uniform composition and you know so the solid which is rejected you know in this case when $K < 1$ now that will be piling up and form a solute rich boundary.

So solute rejected gets piled up and you know and forms a solute rich boundary layer ahead of growth front. So in this case the equilibrium will be existing only at the interface because you will have limited liquid diffusion as well as there is no solid diffusion. So what happens in these cases you will have at the interface you will have solute segregation occurring. So in these cases if you look at you know the you will have you will see that if you have this as this solid which is formed.

Now in this case at liquid you will have this way you have piling up so you know this reason is known as the solute rich boundary layer so you will have liquid you know this is solid and this side you have liquid. So you know from KC_0 to C_0 it will be reaching you know and so if you see the variation of the KC_0 so for the you know solid part from KC_0 to C_0 it will reach and for the liquid part C_0 to C_0/K it will reach.

And this way ultimately it will move and in the end it will also be moving and this will also be moving. So this will be coming to C_0 in this case for solid. So basically this region is characterized by a region of this you know solute rich boundary layer region and in these cases as the condition will be you know for the $D_s T$ or D_L into T so it will be quite lesser than the L square values so that way those will be the conditions.

And initial this will be case of initial transient or so. So these are basically the three cases and again here you know you will have you know there is certain mathematical formulation for finding the steady-state composition profile and it has been shown that it will be $(C_L - C_0)/(C_0/K - C_0) = e^{-(R/DL)z}$. So you know in this case R is the growth rate and you know you will have the z as the distance from the solid liquid interface.

So z will be 0 at you know so when z is 0 at that place your $C_L - C_0$ has the maximum value that is $C_0/K - C_0$. So that is how you get these values and you will have these are the initial transients and you have the final transients in these cases. So there are certain formulas by which you can have the computation of the C_L and C_s so that can be found so we will see these three different cases to understand the solidification mechanism.

You know mode of solidification and associated you know phenomena which results into the different microstructure in the case of the solidification of alloys in our coming lecture. Thank you very much.